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Metal-Catalyzed Alkynylation of Brominated Polyphenylenes. Thermoset Precursors of
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24.

Metal-Catalyzed Alkynylation of Brominated Polyphenylenes. Thermoset Precursors of High Density Monolithic Glassy Carbon

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Abstract:

The functionalization of brominated polyphenylenes with several alkynes is described. The bromide groups on the polymer were replaced with terminal alkynes using a Pd/Cu catalyst system. Substitution of nearly all the original bromide locations was achieved. The functionalized polymers, freely soluble in THF, exhibited high char yields of up to 89% on thermolysis to 900°C under a nitrogen atmosphere. Several of the functionalized polymers, derived from brominated polyphenylenes with approximately equal amounts of *meta*- and *para*-linkages, flowed on heating. The polymer that was functionalized with phenylacetylene exhibited a well-defined melting point at approximately 200°C and flowed to produce a monolithic disk of glassy carbon. The amount of acetylenic crosslinking units in the polymers functionalized with phenylacetylene appears to be directly related to the char yields of the functionalized polymers. Predominantly *meta*-linked brominated polyphenylenes were also functionalized with a number of terminal alkynes and though high char yields of up to 86% were observed, these materials offered no improvements in flow properties. The structure/property relationships and material applications are discussed.

Introduction:

Polymeric carbon materials, produced from the thermolysis of organic polymers in inert atmospheres, have seen numerous applications in the aerospace, electrical, medical implant, and automotive industries.¹ While phenolic resins have been used extensively as thermoset precursors of carbon, these resins typically exhibit 35-40% weight loss on thermolysis and densities of the carbon char are approximately 1.3 g/cc.² Due to the large weight losses and low density chars exhibited by phenolic resins, multiple impregnation cycles (usually 6-7) are required for adequate structural formation. This can greatly raise the cost of the final carbon product. In order to lower the number of impregnation cycles (the cost determining step) necessary for high density carbon preparation, the development of high char yielding materials from alkyne-containing organics has been investigated by many.³ Unfortunately, the difficulty in preparing the alkyne-containing monomers and the explosive nature of the multi-alkynylaromatics^{3h,4} has retarded the rapid development and commercialization of this process. Likewise, *para*-polyphenylene (PPP) has been studied for its applicability as a polymeric carbon precursor because of its high carbon-to-hydrogen ratio and near 80% char yields.⁵ However, PPP does not flow on thermolysis and it is insoluble in all common organic solvents. This has precluded its use in thermosetting materials.

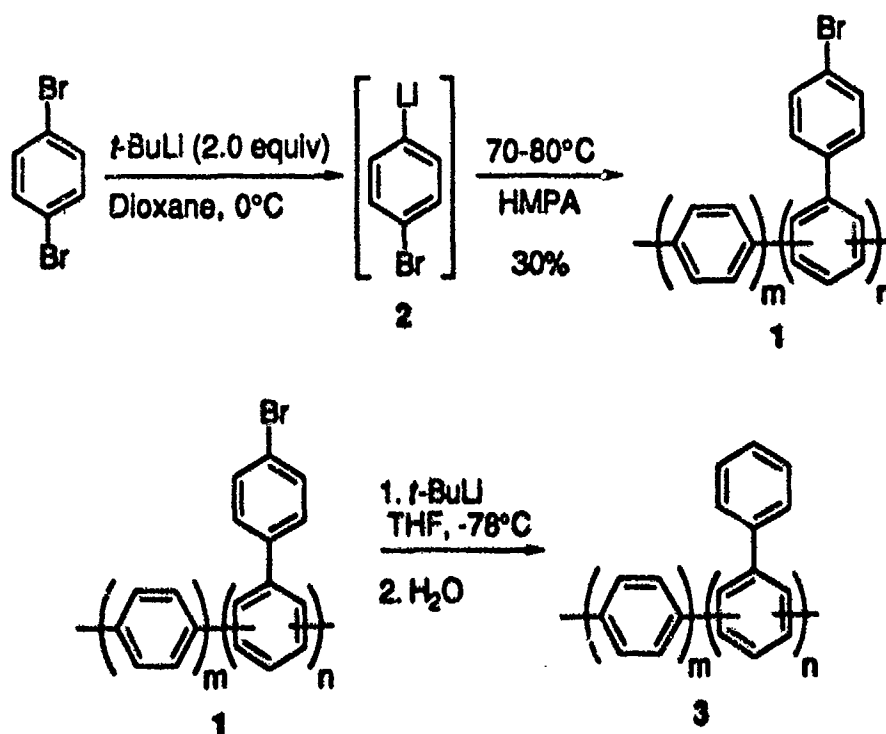
We recently reported the synthesis of alkyne-containing polyphenylenes possessing several features which make them attractive as thermoset precursors of high performance high density glassy carbon materials.⁶ These polymers exhibited 85-90% char yields upon heating in inert atmospheres while the charred material possessed densities of ≥ 1.80 g/cc after one heating cycle (50-900°C). The alkyne-containing polyphenylenes also exhibited a well-defined melting event ($\sim 200^\circ\text{C}$) prior to conversion to carbon which may also offer advantages in fabrication processes. Here we report the detailed results of the preparation of these alkyne-

containing polyphenylenes as well as the thermal properties of these polymers in nitrogen and air atmospheres.

Results and Discussion:

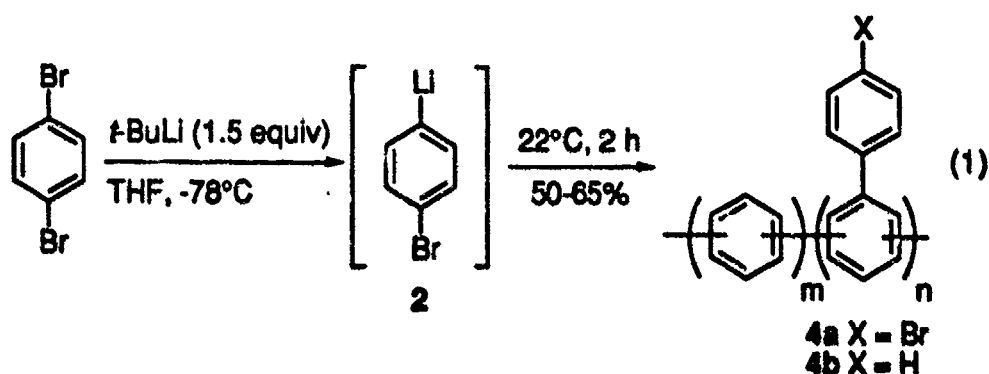
While investigating the thermal properties of predominantly *para*-linked, brominated polyphenylenes **1** prepared in our laboratory using a one pot HMPA promoted polymerization of 1-bromo-4-lithiobenzene (**2**) in dioxane⁷ (Scheme I), we

Scheme I



became interested in using these materials as thermoset precursors to glassy carbon. Although **1** and its debrominated derivative **3** exhibited high carbon-to-hydrogen (C/H) ratios, these predominantly *para*-linked polymers showed low char yields (approximately 50%) on heating during TGA (N₂, 20°C/min) analysis. No melting or softening temperatures were observed by DSC (N₂, 20°C/min) analysis. Visual observation of the charred material after TGA analysis also indicated that no

significant melt had occurred on heating. Due to the absence of any significant melting transitions for polymers 1 and 3, it became apparent that some structural feature of the brominated polyphenylene 1 would need to be changed in order to obtain processible glassy carbon precursors. During studies of the HMPA promoted polymerization of 2, we found that 50-65% yields of ether insoluble (THF soluble) brominated polyphenylenes (4a) could be prepared using THF as the polymerization solvent (eq 1).⁸ Polymer 4a offered several attractive advantages over 1. First, the

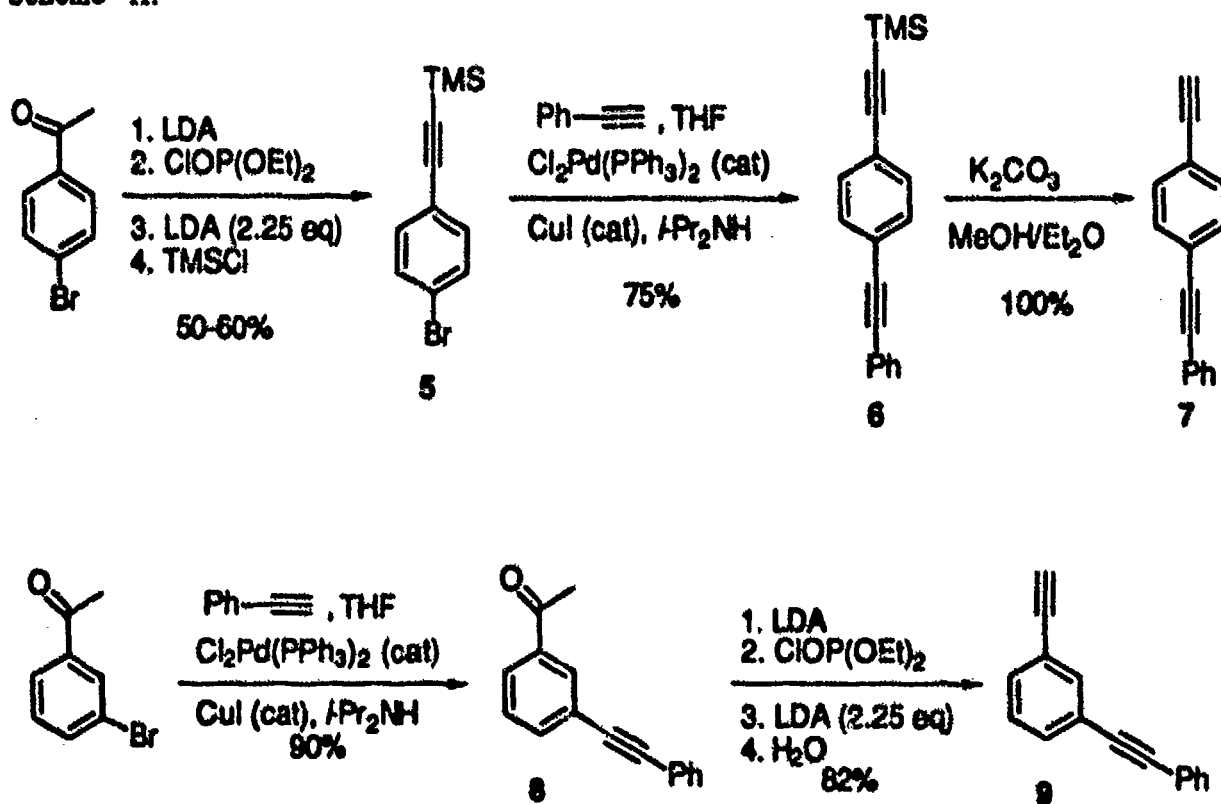


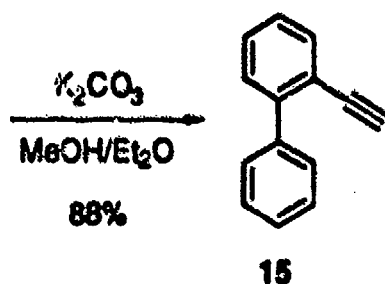
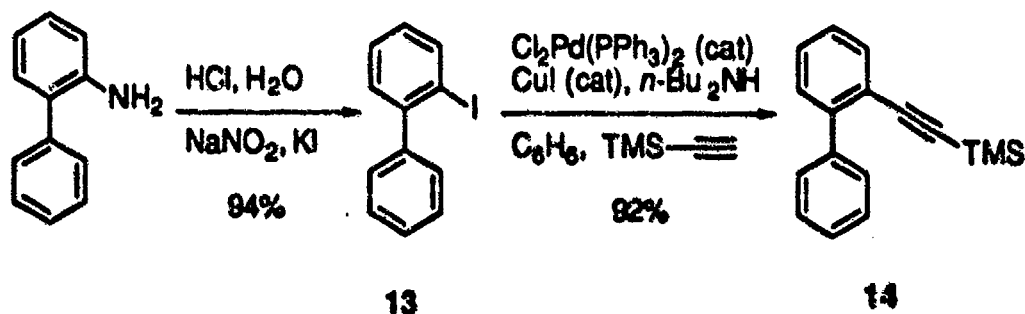
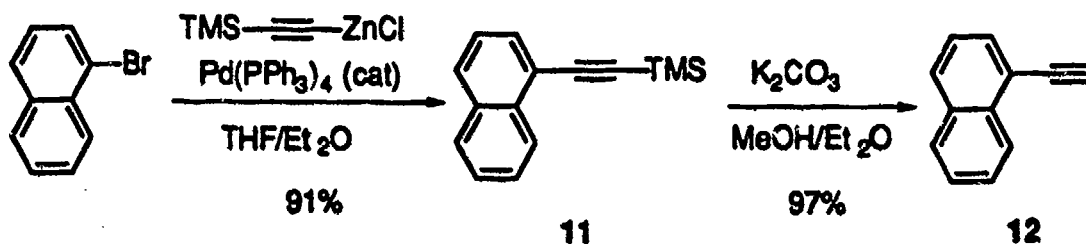
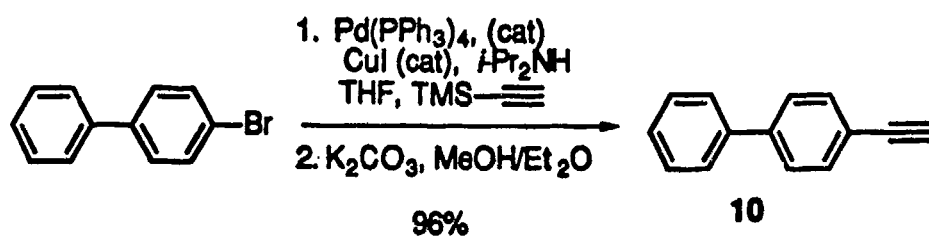
synthesis of 4a did not require the use of the cancer suspect agent HMPA. Second, 4a contained higher amounts of *meta*-linkages which enabled the polymer to melt or flow during thermolysis. The DSC (N₂, 20°C/min) of 4a showed broad endotherms, characteristic of melting events at 152 and 175°C on the first heating scan to 230°C. While the char yield for 4a was only 50% by TGA analysis, the charred material was porous and glossy black which also indicated that the material had flowed during thermolysis. Third, 4a was shown by elemental analysis to contain up to one bromide for every three aryl rings. Since the material was soluble, the bromide groups in the polymer could be used as functionalization sites. Based on the high char yields of other alkyne-containing aromatics,³ we decided to functionalize polymer 4a with a variety of acetylenic groups that would crosslink during thermolysis and reduce the amount of weight loss due to volatilization of the lower molecular weight oligomers.

In order to maintain a processible system, it was important that the acetylenic moiety not crosslink prior to the polymer melt.

Polymer 4a was functionalized with a number of terminal alkynes using the Stephans/Castro-Sonogashira protocol that employs a Pd/Cu-catalyst for cross-coupling of aryl halides and terminal acetylenes.⁹ Phenylacetylene, 1-octyne, and trimethylsilylacetylene were obtained commercially. 1-Ethynyl-4-(phenylethynyl)benzene (7), 1-ethynyl-3-(phenylethynyl)benzene (9), 4-ethynylbiphenyl (10), 1-ethynylnaphthalene (12), and 2-ethynylbiphenyl (15) were prepared using reaction combinations involving the phosphate enolate procedure for acetylene formation,¹⁰ Pd/Cu-catalyzed cross-coupling,⁹ and protodesilylation with K_2CO_3 in methanol/ether (Scheme II).

Scheme II.

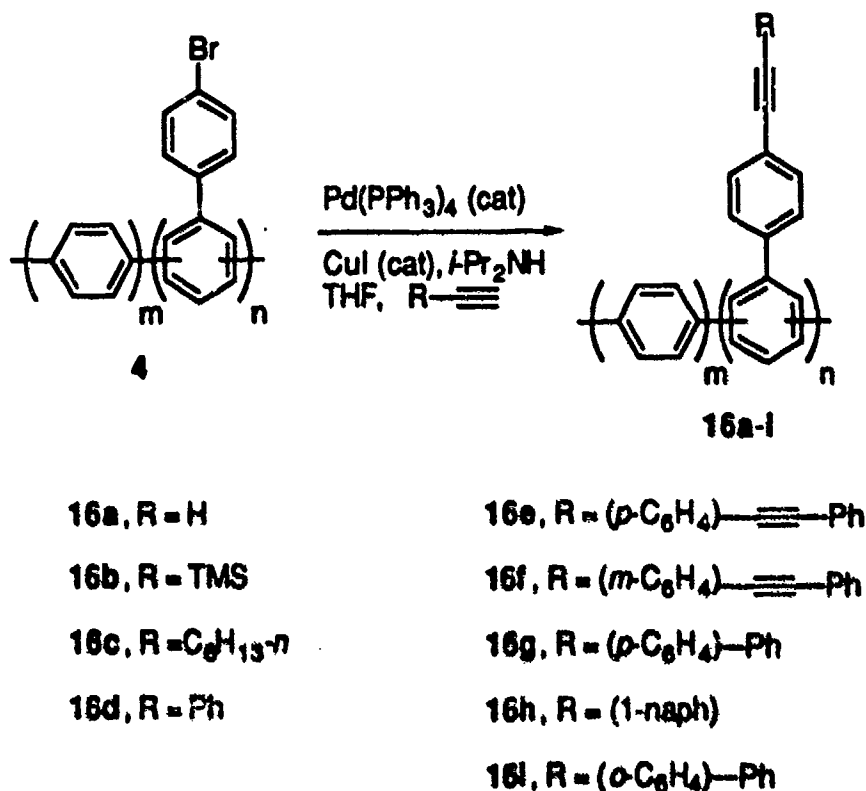




The procedure for coupling the terminal alkynes to polymer **4a** involved treatment of **4a** with the terminal alkyne (3.5 equivalents relative to the amount of Br in **4a**) in a THF solution containing diisopropylamine (3.5 equivalents relative to the amount of Br in **4a**), CuI catalyst (4.0 mol% relative to the amount of Br in **4a**) and a $\text{Cl}_2\text{Pd(PPh}_3)_2$ or $\text{Pd(PPh}_3)_4$ catalyst (4.5 mol% relative to the amount of bromide in **4a**). The ensuing reaction mixtures were stirred at room temperature for 2 h then

heated (60°C for 10 h, 100°C for 5 h) to afford good yields of functionalized polyphenylenes 16b-16l (Figure 1). In most cases, complete bromide substitution

Figure 1.



was achieved as determined by elemental analysis. All of the functionalized polymers were soluble in THF, methylene chloride, and chloroform. The thermal properties of these polymers are shown in Table I.⁶

Several structure/property relationships soon became evident and enabled us to rapidly converge on a suitable thermoset precursor to glassy carbon. Polymer 16a was prepared by addition of tetra-*n*-butylammonium fluoride (TBAF) to 16b in THF at 0°C followed by stirring at room temperature for 1 h. Although 16a exhibited a high char yield (80%), the terminal alkyne was too unhindered and the crosslinking event occurred prior to a well-defined melt or softening point by DSC analysis. The charred material, after TGA analysis was also a black powder, again indicating that no flow

had occurred. The char had a density of 1.59 g/cc.¹¹ Polymers 16b and 16c had internal alkynes and they did exhibit well-defined melts at 140°C by DSC analysis while the thermolyzed material formed glossy black droplets which also indicated that a melting event had occurred. However, the introduction of aliphatic groups decreased the char yields to only 69% and 67%, respectively. Remarkably, by functionalizing 4a (prepared by refluxing 1-bromo-4-lithiobenzene (2) in THF for 2 h) with phenyl acetylene to produce 16d, the char yield increased to 86% at 900°C and the polymer exhibited a well-defined melt at 200°C. Gravity flow of the melted material occurred to form a glossy black monolithic disc which was amorphous by powder XRD confirming that the material was indeed glassy carbon.⁶ The density of the charred product was 1.83 g/cc. Initial data had suggested that no crosslinking events had occurred prior 320°C; however, at 320°C a large exotherm was observable by DSC analysis.⁶ This crosslinking event was 120°C higher than the melting temperature. However, upon closer evaluation of the DSC thermograms, a small exotherm at 220°C was apparent.¹² This would suggest that some crosslinking was occurring soon after the melt. However, the material did indeed flow during the heating process. Interestingly, when we attached phenylacetylene to a predominantly *para*-linked brominated polyphenylene (prepared using the HMPA procedure⁷) the char yield was high (~82%), however, the flow properties on thermolysis were impaired. The charred material was a black powder, therefore, it had not flowed. Thus the unique flow properties of 16d are undoubtedly due in part to the higher amount of *meta*-linkages in this polymer system. When a sample of 16d having $M_w = 2480$ ($M_w/M_n = 3.22$) and a well-defined melt at 180°C (DSC), was purified further by fractional precipitation from methylene chloride with ether, the flow properties of the polymer were impaired. The thermolyzed material was powdery and it had not flowed. The purified product had a higher molecular weight

($M_w = 3500$) and a lower polydispersity ($M_w/M_n = 2.72$). Thus higher molecular weights and lower polydispersities retard the flow properties of 16d.

In an effort to further increase the char yields, additional functionalized polymers (16e-16i) containing high C/H ratios were prepared. From the results in Table I it can be seen that although the char yields were increased to almost 90% for 16e and 16f, the flow properties for these two systems were diminished. No T_m was clearly evident by DSC analysis though T_g s were evident. The materials formed dull gray meshes during thermolysis indicating that some flow had occurred. These meshes were also shown to be amorphous glassy carbon by powder XRD. The densities of the charred products from 16e and 16f were 1.95 and 1.39 g/cc, respectively. Polymers 16g, 16h, and 16i formed glossy black beads during thermolysis and appeared to have similar flow properties to that of 16d. However, 16g and 16i had char yields of only 84% and 78%, respectively. Polymer 16h had a slightly better char yield of 87%. The densities of the charred carbon products from 16g and 16h were 1.52 and 1.55 g/cc, respectively. Thus these polymer systems offer no significant advantages in flow properties or char yields when compared to polymer 16d, moreover, phenyl acetylene, the reagent necessary for 16d, is both inexpensive and commercially available. Furthermore, the density of the charred material derived from 16d was extremely high (1.83 g/cc). This would also lower the cost of fabrication of high performance carbon materials by limiting the number of impregnation cycles to 1-2. Thus 16d appears to be an extremely attractive thermoset precursor of high density monolithic glassy carbon.

Additional studies on the thermal properties of polymer 16d showed a direct correlation between the carbon char yields, position of the *para* band stretch in the FTIR of the functionalized polymer, and the amount of *tert*-butyllithium used to prepare the starting brominated polymer 4a (Table II). As the wave number of the *para* stretch in 16d decreased, the char yields for 16d increased. Likewise, as the

amount of *tert*-butyllithium used to prepare 4a increased, the char yield decreased. The polymers with the highest char yields were derived from the brominated polymers (4a) prepared using 1.5 equivalents of *tert*-butyllithium. Brominated polymers prepared in this manner were shown by elemental analysis to contain 24% bromide or approximately one bromide for every three aryl rings. The position of the *para* band in the FTIR was approximately 809 cm^{-1} . If higher amounts of *tert*-butyllithium (2.0 equivalents) were used to prepare 4a, the amount of bromide in the polymer was reduced to 9% or approximately one bromide for every ten aryl rings. The wave number of the *para* band in polymer 4a also increased to 814-817 cm^{-1} if more *tert*-butyllithium was used.¹³ Based on these results, it appears that if the amount of acetylenic crosslinking units in 16d is reduced, the char yields are lowered accordingly.

TGA (20°C/min) studies in air were also performed on polymer 4a as well as several of the functionalized polymers derived from 4a, namely 4b (prepared by treatment of 4a with *tert*-butyllithium and quenching with water), and 16d-h. The results are shown in Table III. All of the polymers were completely volatilized before 800°C. While the onset of weight loss for the brominated and debrominated polymers 4a and 4b was only 250°C, the polymers 16d-h, functionalized with acetylenic crosslinking moieties, showed no significant weight loss before 400°C. Thus the incorporation of acetylenic groups with high carbon/hydrogen ratios improved the thermal properties of the polymers in both nitrogen and air atmospheres. For comparison, the onset of weight loss in air for PPP prepared by the Kovacic method and phenylated polyphenylenes prepared by Stille is reported to be 550°C. The reported onset of weight loss in air for the Hercules HA-43 resin is 450°C.^{5c}

Predominantly *meta*-linked brominated polyphenylenes prepared from the polymerization of 1-bromo-3-lithiobenzene (17) in THF¹³ (eq 3) were also

functionalized with a number of thermoactive acetylenic crosslinking groups using Pd/Cu catalyzed cross-coupling reactions (Fig II).¹⁰ Surprisingly, these

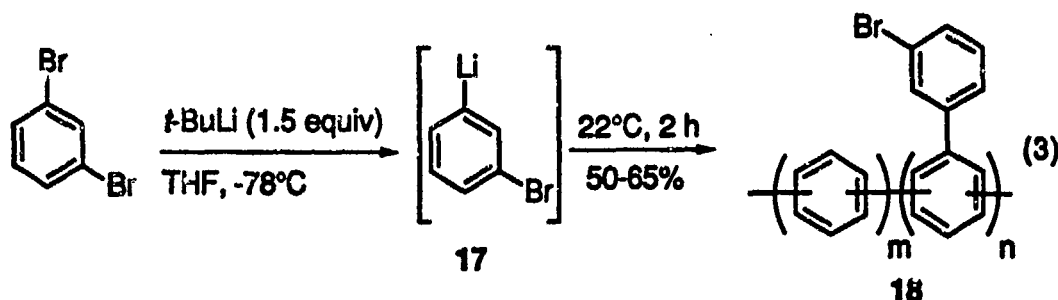
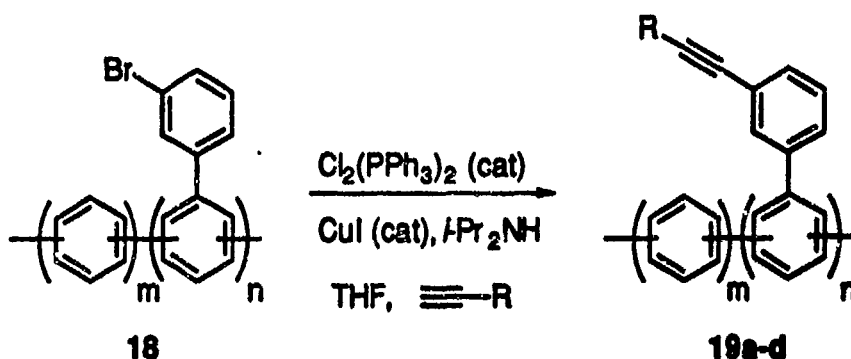


Figure II.



19a R = Ph

19b R = (*p*-C₆H₄)—≡—Ph

19c R = (*m*-C₆H₄)—≡—Ph

19d R = (*p*-C₆H₄)—Ph

predominantly *meta*-linked materials offered no improvements in char yields or flow properties. The lower polydispersities ($M_w/M_n = 1.87$) of the starting brominated polymer 18 may be retarding the flow properties of this system. No melting transitions were observed for polymer 18 by DSC (N₂, 20°C/min) analysis on either the first or second heating runs up to 250°C. These polymers did, however, appear to flow by visual observation of the charred material after TGA (N₂, 20°C/min) analysis

which showed a 59% char yield for 18. The results of the thermal analysis of the functionalized polymers 19a-d are shown in Table IV. A T_g at 180°C was observable for 19a and the charred material appeared as shiny black droplets after TGA analysis. The charred carbon material from 19a had a density of 1.56 g/cc. Polymers 19b and 19c appeared as black powders after TGA analysis. The DSC thermogram of 19c did show an apparent melt at 175°C. Charred polymer 19d appeared as a shiny porous bead with a T_g at 190°C. Carbon materials derived from 19b and 19c had densities of 1.57 and 1.61 g/cc, respectively.

In conclusion, the ability to functionalize the brominated polyphenylenes using Pd/Cu catalyzed cross-coupling methodology has provided an overall two step (polymerization and functionalization) procedure for obtaining thermoset precursors to glassy carbon materials. The low cost of the starting materials, unique flow properties, high char yields of the functionalized polymers, and the high densities of the thermolyzed products make this process attractive for the rapid formation of glassy carbon products requiring high densities.